COLOUR AND BEAUTY AT THE BLACK SEA COAST: ARCHAEOMETRIC ANALYSES OF SELECTED SMALL FINDS FROM HISTRIA

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Abstract. This paper reports the chemical composition of eight archaeological small finds excavated at Histria, Romania. The bulk non-destructive analyses were performed using Prompt Gamma Activation Analysis (PGAA) at the Budapest Neutron Center (BNC). Different compositional patterns were evidenced, indicating the raw materials used in the manufacturing of these small objects.

Key words: Histria, PGAA, ancient glass

1. INTRODUCTION

Histria (Istros) is one of the most significant archaeological sites from Romania. Founded as a colony of the Greek city of Miletus during the second half of the 7th c. BC, *Histria* played an important political and economic role in the Black Sea region until the beginning of the 7th c. AD, when the city was abandoned. During the 1st c. BC *Histria* was integrated in the Roman Empire, becoming part of the Roman trade network [1-2].

During the last century, the archaeological research at *Histria* brought to light a large number of glass finds – vessels, window panes, adornments – which were either imported or possibly shaped on the spot − see *www.cimec.ro/web-histria*.

Particularly remarkable are several small glass objects, such as beads and inlays of jewelry items. Despite the intense archaeological research at this site, the proper documentation and publication of the vitreous items discovered at *Histria* started only during the last twenty years [3-8].

A project supported by the University of Bucharest (2013-2016 and 2017-2021) allowed the opening of a new sector at *Histria* Sector − Acropola Centru-Sud (ACS)/Acropolis Centre-South Sector − located in the southern part of the city, in an area undisturbed by the earlier excavations [9].

Taking into account the relative scarcity of archaeometric data on glass finds brought to light on the territory of Romania [10-18], during the last years a project aiming the characterization of representative glass finds discovered in archaeological sites from the western coast of the Black Sea coast, was initiated.

This paper reports the bulk chemical composition of eight small objects excavated at *Histria*, Romania, in the ACS Sector, in a Late Roman/Early Byzantine building dated to the 6th c. AD. The analyses were performed using Prompt Gamma Activation Analysis (PGAA) technique at the Budapest Neutron Centre (BNC) [19]. Based on the compositional data, several conclusions about the raw materials and manufacturing techniques were obtained, thus increasing the knowledge on material finds from *Histria*, and, more generally, well on the use of glass on the Black Sea coast during the Antique period.

2. MATERIALS AND METHODS

2.1. SAMPLE DESCRIPTION

The eight samples reported in this paper are shown in Figure 1.

Sample Histria-2 is a diminutive transparent amber-yellow oblong glass bead, whose shape reminds of a wheat grain. The bead has a longitudinal perforation which is very large compared to the small body. This item is almost completely preserved, only one of its ends being slightly broken.

Sample Histria-5 is a large opaque dark bead, discovered intact in a good state of preservation. At the moment of its finding and after the first washing, the surface of this bead appeared to be dark blue. Cleaning this bead in an ultrasonic bath showed that its body is in fact black, the bluish tinge being just the result of the weathering phenomena that took place during the burial. The bead is decorated with light blue undulating thin lines and yellow dots ("eyes"). The dating of this bead raises some difficulties, as this type of bead (*Grosse Perle polychrome*) could be equally assigned either to the 6th – 5th c. BC or to the 5th – 6th c. AD [20-21].
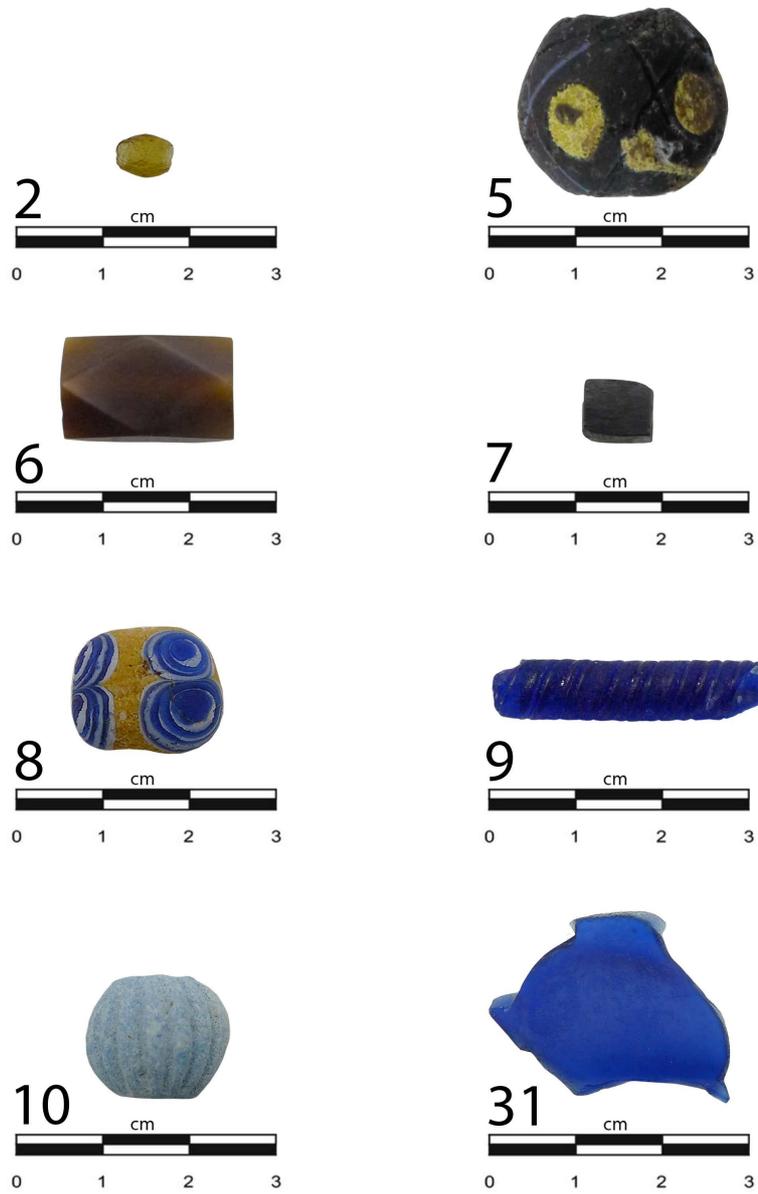
Fig. 1 – Photos of the *Histria* samples.

Sample Histria-6 is a well-finished polyhedral amber bead with a longitudinal perforation. The high transparency and clarity of the material, as well as the lack of inclusions, suggested the assignment of this find to the category of glass beads. This type of bead made of either glass or gemstone was a quite familiar presence in the contexts dated to the Roman period, being frequently discovered in Sarmatian graves – e.g. group V A4 from [22] and type IV from [23].

Sample Histria-7 is a small opaque black cube of unknown function. Its dimensions and shape led to the hypothesis that it could have been a mosaic *tessera*, made either of black glass or, more likely, considering its luster and opacity, of a lithic material.

Sample Histria-8 is a half of a bead with yellow body and blue "eyes" decoration. The section was covered with the same kind of crust as the external convex surface indicating that the find was buried in soil in fragmentary condition for a long period of time. So far, the closest analogy came from a male pit grave from Thermi, Greece, dated to 500–450 BC [24].

Sample Histria-9 is a fragment from a twisted cobalt blue glass bar identified as a stirring rod (Isings form 79) [25]. Such glass objects were in use during the 1st – 2nd c. AD [21, 25].

Sample Histria-10 is a light turquoise opaque bead, spherical in shape and decorated with ribs. This item, intact and in a good state of preservation, was tentatively considered from the moment of its discovery as being made of faience. As with many other types of beads, the ribbed ones seem to have been in and out of fashion for quite some time, so they tend to be less chronologically expressive. A very good analogy for this item is offered by some finds from the House of Menander, Pompeii: six spherical beads with ribs (*costolature*) made of light turquoise "vitreous paste", dated to the second half of the 1st c. AD [26]. Ribbed beads probably made of faience and with deteriorated glaze were also recovered from some Late Roman and Byzantine sites from Israel [27].

Sample Histria-31 is a fragment from a cobalt blue vessel, namely a bulbous *unguentarium* dated to the Early Roman period (1st – 2nd c. AD) [28].

2.2. EXPERIMENTAL

The PGAA measurements to determine the bulk elemental composition of *Histria* finds were performed at BNC. The PGAA facility is installed on a horizontal cold neutron beam of the Budapest Research Reactor. The current state of the Budapest PGAA experimental setup is described in great detail in [29].

The thermal equivalent beam intensity was $9.6 \times 10^7 \, cm^2 \cdot s^{-1}$. The quantitative analysis is based on the detection of gamma photons emitted in (n,γ) reactions, using an HPGe detector surrounded by a BGO scintillator annulus. The prompt-gamma spectra were collected by a 64k MultiChannel Analyzer and evaluated with the Hypermet-PC software.

In principle, PGAA is capable to detect all chemical elements, but with very different sensitivities. The method is particularly useful for the detection of H, B, Cl and some rare-earth elements, which have relatively high neutron absorption cross-section. The quantitative analysis is based on the prompt k_0 principle [30-31].

One of the greatest advantages of PGAA is that it provides the bulk average composition of the analyzed sample in a completely non-destructive way. Furthermore, the induced radioactivity diminishes quickly after the irradiation and the artefacts can be quickly returned to the archaeologists and curators after the PGAA experiments. However, glass samples that contain sodium should be kept in the laboratory for 2-3 days cooling, because of the short-lived ^{23}Na ($T_{1/2}$ = 14.96 h).

The Budapest PGAA station has been extensively used to characterize a wide range of cultural heritage objects. Among others, the method was successfully applied for the characterization of ancient glass finds [32-34] and obsidian samples [35]. The accuracy of PGAA method has been assessed by measuring a series of reference glasses − for more details on this topic, see [33-34].

The samples were irradiated for 1200–58000 s with an external cold neutron beam and the spectra were acquired to obtain statistically significant peaks for all elements of interest – see below. The cross-section of the external neutron beam varied between 10 mm^2 and 400 mm^2. In most cases, the entire volume of the object was irradiated with the neutron beam.

Before the experiment all objects were washed with water and gently brushed to remove the superficial dirt and soil deposits. Several samples, despite these cleaning procedures, retained some visible stains onto their surfaces. Moreover, thin layers of weathering products (maximum 100 μm thick) cover the surface of any ancient vitreous object that stayed buried in ground for millennia, with composition slightly different from the one of the underlying glass. As PGAA is a bulk analytical technique, the weathered glass layers and the superficial deposits have practically negligible contributions to the overall chemical composition.

Using PGAA it was possible to quantify the following major, minor and trace components: H, B, Na, Al, Cl, Si, Ti, K, Ca, Mn, Fe, Sm and Gd in all samples, and Mg, S, Co, Cu, Sb, Nd and Pb only in certain objects. The quantitative results expressed in wt%, and normalized to 100 wt%, as well as the detection limits, are given in table 1 – to visualize this table, the reader is referred to the online version of the paper. All concentrations are expressed as oxides, except for Cl that is given in elemental form.

For quantitative PGAA, the most important source of uncertainty is related to the peak area determination, i.e. the counting statistics [30].

In the following discussion, not only the major and minor elements of the vitreous matrix (Si, Na, Ca, Pb, K, Mg, Al, Ti, Fe, Mn, and Cl) were considered to obtain some information about the raw materials and manufacturing techniques, but also some trace-elements, such as Co, Cu and Sb, significant for the chromophores and opacifiers. In some samples, manganese was found close to the

detection limit (i.e. 200 ppm MnO), thus these values should be considered only as indicative for the presence of this element. Concentrations of several trace elements resulting from PGAA (H, B, Sm, Nd, Gd) were also reported in table 1, but they were not taken into account in the discussion of the results.

3. RESULTS AND DISCUSSIONS

Three out of the eight analyzed samples, namely Histria-2, Histria-9 and Histria-31 were clearly identified as soda-lime-silica glasses, as indicated by the average concentrations of soda (17.27 ± 1.33) wt% Na_2O, lime (7.33 ± 2.33) wt% CaO, and silica (67.59 ± 1.98) wt% SiO_2. The magnesia (MgO) and potash (K_2O) content in these samples are ≤ 1.5 wt%, showing that natron was the mineral flux employed in their making [36]. While potash was quantitatively determined in all samples, in sample Histria-9, magnesia was under the detection limits of the PGAA setup, which is estimated to be approximately 1.0 wt% MgO.

The amber yellow bead Histria 2 contains 2300 ppm SO_3 and 3170 ppm Fe_2O_3; most likely, this sample owes its color to an iron-sulphur compound [37-38]. Remarkable for this sample is the reduced manganese concentration (480 ppm MnO). Manganese compounds usually act as oxidizers, while the generation of amber color requires reducing conditions [37-38].

The detection limits for CoO for the PGAA setup are estimated to 100 ppm. The dark blue glass samples, Histria-9 and Histria-31 contain cobalt in amounts above this detection limit, i.e. 572 and 1151 ppm CoO, respectively. As cobalt is a strong chromophore, the addition of low amounts of cobalt compounds to the glass batch was enough to induce the particular dark blue color of these glass fragments [39]. These samples also contain copper above the detection limits, but in relatively low amounts (~ 1500 ppm CuO), not enough to play a significant role in the coloring processes. Most likely, the presence of the copper in these samples is related to the cobalt ore, as during the Early Roman period, the cobalt colorant used in glass manufacturing was actually a mixture of iron, cobalt and copper oxides [39].

Considering the overall compositional pattern – major and minor elements, particularly the concentrations of Na, Ca, Ti, Fe, and Mn oxides – the assignation of these three soda-lime-silica samples to well-known glass chemical groups from the archaeometric literature, in particular, to the *Groupes* and *Séries* introduced by Foy and colleagues [40-41], turned out to be rather problematic, also taking into account the chronologic details. The comparison terms are given in Table 1.

Thus, sample Histria-2 contains relatively little Na_2O (15.74 wt%) suggesting that glass used in its making originated in some Levantine workshops [38, 40].

In particular, the amber yellow glass bead Histria-2 has a composition reminiscent of the typical Roman Imperial glass, also known as Roman Naturally

Colored Blue Green Yellow 2 (RNCBGY2) as defined in [43], manufactured using mature sands from the Syro-Palestinian coasts of the Mediterranean Sea, with low contents of Ti, Mn and Fe.

On the other hand, its very high lime content (9.95 wt% CaO) suggested a possible similarity with *Série 3.3* of Foy [40], a chemical group dated to the Late Roman period (7th c. AD), also of Levantine origin.

However, as noticed by Paynter and Jackson, amber glass was rarely encountered in the Roman world after the 2nd c. AD [38]; therefore the similarity with *Série 3.3* of Foy is questionable.

An alternative interpretation for the relatively high lime (9.95 wt% CaO) and magnesia concentrations (1.17 wt % MgO) is that these components derived from the carbonatic soil deposits, rich in calcite and dolomite, that were present on the surface and in the perforation of this bead when performing the PGAA analyses. The relatively low chlorine content (0.86 wt% Cl) might be the consequence of heating the glass when fashioning this small object – chlorine is a volatile element.

In any case, Histria-2 bead seem to have been made from glass originating in a Levantine workshop, using mature sands and well-controlled manufacturing conditions, i.e. reducing firing and no intentional addition of any manganese minerals.

Considering its very low content of manganese (300 ppm MnO) and the relatively high concentration of antimony (6400 ppm Sb_2O_3), Histria-9 sample seems to have a compositional pattern typical for an object manufactured from Sb-decolorized glass (i.e. pertaining to *Groupe 4* of Foy) [41], whose blue coloration was produced by the addition of a Co-mineral to the glass batch [39]. Such a process might have taken place in secondary workshops that used Sb-decolorized glass as raw material.

We must also consider the possibility of RNCBGY2 glass, i.e. the typical Imperial Roman glass that was colored by adding some cobalt minerals poor in manganese and rich in antimony [39].

Another explanation is that sample Histria-9 was manufactured from glass belonging to *Série 3.2* of Foy [40], to which some cobalt compounds were added as chromophores. However, one must be cautious with this last hypothesis, as the artefacts belonging to *Série 3.2* of Foy were dated to the 5th–6th c. AD [40], while the dating based on stylistic grounds of this stirring rod was restricted to the 1st–2nd centuries AD.

The vessel fragment Histria-31 can be assigned to *Série 2.1* of Foy by taking into account its relatively high content of soda (17.98 wt% Na_2O), lime (6.60 wt% CaO), iron (1.707 wt % Fe_2O_3), manganese oxide (0.592 wt% MnO), and titanium oxide (0.186 wt% TiO_2). However, glass finds belonging to this chemical group, originating from Egyptian workshops, were dated to the Late Roman period (namely, to the 5th–6th centuries AD) [40], in contradiction with the stylistic dating of this particular object – namely, to the 1st–2nd centuries AD.

Histria-8 is an opaque yellow bead with dark blue circular motifs ("eyes"). Because of the underlying principle of PGAA, a bulk analytical technique, it was impossible to separate the gamma rays emitted by the blue glass decoration from the ones emitted by the yellow glass body.

The main feature of Histria-8 is the relatively high lead content (9.31 wt% PbO), accompanied by a significant amount of antimony (1.69 wt% Sb_2O_3). The presence of these two elements suggests that the opaque yellow glass was made by using a lead antimonate compound, most likely $Pb_2Sb_2O_7$ [42 and references therein]. The lead antimonate deliberatively added during the manufacturing process not only provided the yellow color and opacity, but due to the relatively high lead content, also increased the workability of glass, allowing an easier shaping of this small decorative object.

The cobalt content (300 ppm CoO) of Histria-8 sample reflects the use of a cobalt mineral to provide the blue color of the glass decoration ("eyes").

Considering its compositional pattern (3.45 wt% PbO, 15.34 wt% Na_2O and 57.73 wt% SiO_2), a similar discourse can be put forward for Histria-5 multicolored bead – or at least up to a certain point. As no antimony or tin were detected in this object (the detection limits of the PGAA setup are 0.1 wt% Sb_2O_3 and 0.5 wt% SnO), the data reported in this paper are not enough to allow the identification of the yellow chromophore used to make the yellow "eyes": lead antimonate or lead stannate [42 and references therein].

The high concentration of iron (7.468 wt% Fe_2O_3) provides the explanation for the black color of this bead [44], while the cobalt traces (240 ppm CoO) originate in the thin blue trails decorating the surface.

The high concentrations of alumina (4.07 wt% Al_2O_3) can be related to the employed raw materials – most likely, Histria-5 bead was produced using sands different from the ones used to make the other objects discussed in this paper, possibly of Asian/Indian origin [45].

Based on the high content of silica (98.78 wt% SiO_2) and the particular amber brown color, sample Histria-6 is most likely a carnelian and not a glass bead.

The high iron content (90.421 wt% Fe_2O_3) in the black tessera Histria-7, suggests that this is an object made of an iron mineral and definitely not a piece of opaque black glass.

The overall compositional pattern of sample Histria-10 confirms that we are dealing with a faience bead – statement supported by its low sodium content (3.74 wt% Na_2O), balanced by a relatively high silica concentration (86.97 wt% SiO_2). Its lime, magnesia and potash content are also relatively reduced: 1.05 wt% CaO, 1.71 wt% MgO, and 1.67 wt% K_2O, respectively. In any case, this is definitely not a compositional pattern typical for ancient glass. Most likely, this bead was made somewhere in Egypt by mixing high amounts of quartz with small amounts of lime, feldspar, alkali and alumina, by using raw materials and a technology completely

different from the one used in glass making [46-48]. The copper content (1.32 wt% CuO) provides the explanation for the turquoise green color of this bead.

As the PGAA results confirmed that this object is a faience bead, this information was useful to restrict its dating, considering that the production of faience beads in Egypt had ceased by the 3rd c. AD [49-50].

By studying the data reported in this paper, it is obvious that further analyses using other methods, e.g. X-ray diffraction (XRD), SEM (Scanning Electron Microscopy) and/or Laser-Ablation Inductively Coupled Plasma (LA-ICP-MS) are necessary to fully characterize the following samples: the gemstone Histria-6 (most likely a carnelian); the black mosaic tessera Histria-7, probably made from a black iron mineral, and sample Histria-10, identified as a faience bead. The same applies to the composite eye beads Histria-5 and Histria-8, objects made of glass of different colors, and for which PGAA, a bulk method, is definitely not the most suitable analytical approach, despite its non-destructive character, which otherwise is an extremely attractive feature when analyzing cultural heritage objects.

4. CONCLUSIONS

The chemical composition of eight archaeological small finds discovered at *Histria*, Romania, obtained using the PGAA technique at the Budapest Research Reactor were reported in this paper. Based on the information obtained using this fully non-destructive and non-invasive bulk analytical technique, some conclusions regarding the nature, the raw materials and the manufacturing of these objects were obtained. The chromophores and opacifiers (iron and cobalt, and antimony compounds, respectively) used in the making of the vitreous objects were also identified. Trials to assign the raw glass to some primary workshops (Levantine or Egyptians) were made, too. This research is the first step in an on-going project aiming an extensive archaeometric characterization of the vitreous finds discovered in various archaeological sites from the Black Sea coast. More analyses on other glass fragments or using different analytical techniques on the objects reported in this paper are expected to take place in the near future.

5. ACKNOWLEDGMENTS

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Table 1

PGAA results on Histria samples - all concentrations expressed in wt%, empty cells mean below the detection limits

SAMPLE	Oxide/El [wt%]	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	H_2O	SO_3
	Detection limits	*0.1*	*0.050*	*0.50*	*0.050*	*0.020*	*1.00*	*1.00*	*0.01*	*0.10*	*0.090*	*0.10*
Histria-2	amber yellow	**66.1**	**0.070**	**2.80**	**0.317**	**0.048**	**1.2**	**9.95**	**15.74**	**0.93**	**1.763**	**0.23**
Histria-5	black with thin blue lines and yellow eyes	**57.7**	**0.214**	**4.07**	**7.468**	**1.305**	**1.5**	**5.75**	**15.34**	**1.01**	**0.625**	**0.24**
Histria-6	amber brown	**98.8**							**0.07**	**0.05**	**1.050**	
Histria-7	black	**4.8**	**0.581**		**90.421**	**0.122**				**0.29**	**3.614**	
Histria-8	yellow with blue eyes	**64.2**	**0.075**	**1.97**	**1.078**	*0.021*		**6.51**	**12.78**	**0.35**	**0.553**	**0.28**
Histria-9	blue	**69.8**	**0.086**	**1.81**	**0.796**	**0.030**		**5.46**	**18.09**	**1.10**	**0.496**	**0.33**
Histria-10	turquoise green	**87.0**	**0.056**	**1.72**	**0.368**		**1.7**	**1.05**	**3.74**	**1.67**	**0.457**	**0.47**
Histria-31	blue	**66.9**	**0.186**	**1.98**	**1.707**	**0.592**	**1.2**	**6.60**	**17.98**	**0.86**	**0.444**	**0.37**
Histria-2	amber yellow	**66.1**	**0.070**	**2.80**	**0.317**	**0.048**	**1.2**	**9.95**	**15.74**	**0.93**	**1.763**	**0.23**
Histria-9	blue	**69.8**	**0.086**	**1.81**	**0.796**	**0.030**		**5.46**	**18.09**	**1.10**	**0.496**	**0.33**
Histria-31	blue	**66.9**	**0.186**	**1.98**	**1.707**	**0.592**	**1.2**	**6.60**	**17.98**	**0.86**	**0.444**	**0.37**
AVERAGE		*67.6*	*0.114*	*2.20*	*0.940*	*0.223*	*1.2*	*7.33*	*17.27*	*0.96*	*0.901*	*0.31*
STDEV		*1.98*	*0.063*	*0.53*	*0.706*	*0.319*	*0.004*	*2.33*	*1.33*	*0.12*	*0.747*	*0.07*
Histria-2	amber yellow	**66.1**	**0.070**	**2.80**	**0.317**	**0.048**	**1.2**	**9.95**	**15.74**	**0.93**		
Serie 3.3 Foy		*70.94*	*0.080*	*3.00*	*0.520*	*0.010*	*0.67*	*8.48*	*14.65*	*0.69*		
RNCBGY2		*70.60*	*0.100*	*2.50*	*0.400*	*0.500*	*0.50*	*7.70*	*16.10*	*0.80*		
Histria-9	blue	**69.8**	**0.086**	**1.81**	**0.796**	**0.030**		**5.46**	**18.09**	**1.10**		
Groupe 4 Foy		*71.00*	*0.060*	*1.94*	*0.340*	*0.020*	*0.43*	*5.56*	*19.05*	*0.42*		
RNCBGY2		*70.60*	*0.100*	*2.50*	*0.400*	*0.500*	*0.50*	*7.70*	*16.10*	*0.80*		
Serie 3.2 Foy		*68.07*	*0.090*	*1.92*	*0.700*	*0.950*	*0.65*	*6.99*	*18.79*	*0.44*		
Histria-31	blue	**66.9**	**0.186**	**1.98**	**1.707**	**0.592**	**1.2**	**6.60**	**17.98**	**0.86**		
Serie 2.1 Foy		*64.42*	*0.160*	*2.54*	*1.350*	*1.600*	*1.23*	*7.80*	*18.50*	*0.79*		

Table 1
PGAA results on Histria samples - all concentrations expressed in wt%, empty cells mean below the detection limits

SAMPLE	Oxide/El [wt%]	B_2O_3	CoO	CuO	Sb_2O_3	Nd_2O_3	Sm_2O_3	Gd_2O_3	Cl	PbO	SnO
	Detection limits	*0.00005*	*0.010*	*0.050*	*0.10*	*0.001*	*0.00005*	*0.00005*	*0.003*	*1.60*	*0.5*
Histria-2	amber yellow	**0.05403**				**0.007**	**0.00011**	**0.00017**	**0.86**		
Histria-5	black with thin blue lines and yellow eyes	**0.02862**	**0.024**	**0.249**			**0.00018**	**0.00021**	**0.94**	**3.45**	
Histria-6	amber brown	**0.05499**							**0.00**		
Histria-7	black	**0.04187**					**0.00199**	**0.00301**	**0.10**		
Histria-8	yellow with blue eyes	**0.00486**	**0.030**		**1.69**	**0.011**	**0.00011**	**0.00015**	**1.12**	**9.31**	
Histria-9	blue	**0.03347**	**0.057**	**0.150**	**0.64**		**0.00009**	**0.00013**	**1.09**		
Histria-10	turquoise green	**0.00106**	**0.007**	**1.320**		**0.002**	**0.00011**	**0.00011**	**0.45**		
Histria-31	blue	**0.00005**	**0.115**	**0.140**		**0.003**	**0.00013**	**0.00012**	**0.90**		
Histria-2	amber yellow	**0.05403**				**0.007**	**0.00011**	**0.00017**	**0.86**		
Histria-9	blue	**0.03347**	**0.057**	**0.150**	**0.64**		**0.00009**	**0.00013**	**1.09**		
Histria-31	blue	**0.00005**	**0.115**	**0.140**		**0.003**	**0.00013**	**0.00012**	**0.90**		
AVERAGE		*0.02918*	*0.09*	*0.15*			*0.00011*	*0.00014*	*0.95*		
STDEV		*0.02725*	*0.04*	*0.01*			*0.00002*	*0.00002*	*0.12*		

Histria-2	amber yellow
Serie 3.3 Foy	
RNCBGY2	

Histria-9	blue		0.64
Groupe 4 Foy			*0.63*
RNCBGY2			
Serie 3.2 Foy			

Histria-31	blue
Serie 2.1 Foy	